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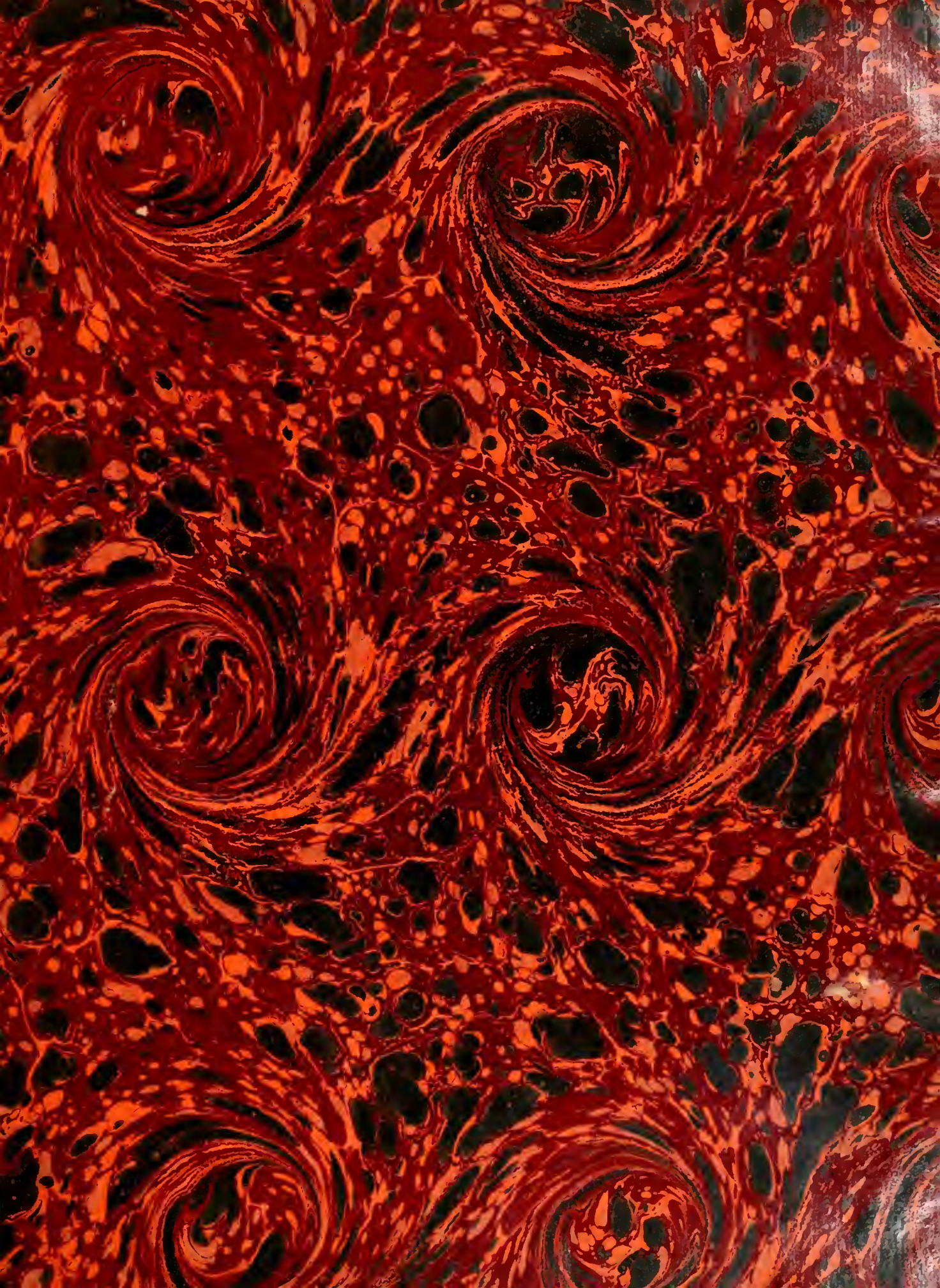

I. PREPARATION OF NITRILES

II. CATALYTIC PREPARATION OF NITRILES

DISSERTATION

Submitted to the Board of University Studies of

the Johns Hopkins University in conformity

with the Requirements for the Degree of

Doctor of Philosophy,

by

George Dudley Van Epps

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I. PREPARATION OF NITRILES

-:-

INTRODUCTION

For the preparation of nitriles we have had the old method of Letts[1] as improved by Krüss,[2] which was to heat an acid, such as benzoic acid, with lead sulphocyanate. This method was easy to carry out and gave fair yields. Reid[3] greatly improved this method by substituting the zinc salt of the acid for the free acid, and obtained excellent yields of benzonitrile and of other aromatic nitriles. The present work was taken up to test the applicability of Reid's method to the preparation of aliphatic nitriles.

The preparation of acetonitrile has been studied most extensively on account of the importance and the availability of acetic acid. Various methods of heating have been experimented with. Lead and zinc salts of acetic, propionic, butyric, isovaleric, stearic, phenylacetic, phenylpropionic, cinnamic and terephthalic acids have been studied. Ca, Cu, Sn, Mn, Ni, Co, Mg, Sr, Ba and Fe acetates have been tried. In most of the experiments the mixtures have been heated in plain glass retorts, while in some cases an iron retort, with and without vacuum, has been used.

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1. Ber. d. chem. Ges. 5, 669 (1872).
2. Ibid., 17, 1766 (1884).
3. Am. Chem. Jour. 43, 162 (1910).

HISTORICAL

E. A. Letts[1] of London, in 1872, studied the action of potassium sulphocyanate on acids. In case of acetic acid, he could not obtain the nitrile, but with isobutyric acid and valeric acid he found both amide and nitrile, the amide being the main product. With benzoic acid the nitrile was almost the sole product, only traces of the amide being found.

Pfankuch[2] heated barium benzoate with excess of barium sulphocyanate and got benzonitrile but mixed with large quantities of other products. Barium acetate and barium sulphocyanate gave similar results, the other products being in excess of the acetonitrile.

Kekulé[3] next took up the question.

G. Krüss[4] complained of the yield in Letts' process and improved the method by substituting lead sulphocyanate for the potassium salt. Krüss gives the equation:

$$2C_6H_5COOH + Pb(CNS)_2 = 2C_6H_5CN + PbS + H_2S + 2CO_2$$

He reported a yield of 50 to 55 grams of benzonitrile from 100 grams of benzoic acid, or double what he was able to obtain by the method of Letts.

Reid[5] studied this reaction quantitatively and showed that it is not represented correctly by the equation given.

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1. Ber. d. Chem. Ges. 5, 669 (1872).
2. J. prakt. Chem. (2), 6, 97 (1873).
3. Ber. d. Chem. Ges. 6, 111 (1873).
4. Ibid., 17, 1766 (1884).
5. Am. Chem. Jour. 43, 162 (1910)

He concluded that the nitrile is formed by interaction between the lead sulphocyanate and the lead salt of the organic acid, this salt being formed by reaction between the free acid put in and a part of the lead sulphocyanate. This led to a substitution of the previously prepared salt of the organic acid for the free acid, and to extended experiments with different salts, the conclusion being that the best yield is obtained when the zinc salt of the organic acid is used. Reid's method left little to be desired in the preparation of benzonitrile and other aromatic nitriles both as to yield and convenience of work but was not extended to aliphatic.

MATERIALS

Lead Sulphocyanate was prepared by precipitation from lead nitrate and ammonium sulphocyanate. The precipitate was washed well with water, then twice with alcohol, and then dried in air. When air-dried it was further dried in air-bath at temperatures above 120° C. The salt is at first pure white in color but turns yellow on standing some time. The salt blackens a little when dried in air-bath but not much harm is done, as a little more than the theoretical amount being always used. For the later experiments five pounds of the salt were specially prepared by a well-known firm.

Zinc Sulphocyanate was prepared by boiling ammonium sulphocyanate with excess of zinc hydroxide until ammonia ceased to come off, filtering hot and evaporating to crystallization. The crystals were pressed out on a porous plate and centrifuged. It was found difficult to dry this salt in air-bath as it fuses easily, foams readily and gives off strong odor at low temperatures. The fused salt is somewhat hydroscopic.

Copper Sulphocyanate was prepared by mixing copper sulphate and ammonium sulphocyanate and reducing the black precipitate of cypric sulphocyanate formed by means of sulphur dioxide. The gray precipitate of cuprous sulphocyanate was washed with water and dried in air-bath. It turned pale

yellow in color.

Potassium Sulphocyanate, Lead Acetate, Copper Acetate, Barium Acetate and Basic Ferric Acetate used were the commercial salts.

Zinc Acetate, Calcium Acetate, Zinc Butyrate, Zinc Propionate and Zinc Isovalerate were prepared by boiling the corresponding acids with excess of carbonate of the metal, filtering hot and evaporating to crystallization. The latter three salts were dried over sulphuric acid in vacuum several days, the others in air-bath.

Stannous Acetate, Manganese Acetate, Nickel Acetate, Cobalt Acetate, Magnesium Acetate and Strontium Acetate were made by C. A. F. Kahlbaum.

Zinc Stearate, Lead Phenyl Acetate, Zinc Phenyl Acetate, Lead Cinnamate, Zinc Cinnamate, Zinc Hydrocinnamate, Lead Benzoate and Zinc Terephthalate were prepared by double decomposition from the neutral ammonium or sodium salts of the acids and lead nitrate or zinc sulphate. All these salts were dried in air-bath at 120° C.

METHODS OF WORK.

The following methods of work were tried:

1. Iron retort, with or without vacuum.
2. Plain glass retort.
3. Short straight tube, heated with a luminous flame.
4. Long straight tube heated in brass block.

In each experiment the dry powders were well mixed before heating. In no case was much trouble caused by foaming except in the single case when zinc sulphocyanate was used. In the second and third methods the burner was held in the hand and, during the first part of the reaction, the heat was applied to the side of the plain retort or under the mixture in the straight tube nearest the mouth so as to keep the reaction under control. The time of heating varies from thirty minutes to four hours, and in two cases seven hours, depending upon the amount of materials used. A single Bunsen burner was sufficient. The iron retort was heated by a ring burner and the reaction completed with a Bunsen burner. The brass block was heated by two Bunsen burners. Whichever method is used, when the heat is applied the mass melts and blackens and bubbles of gas and fumes begin to come off at once. In some experiments the nitrile began to drop from the end of the retort neck within a few minutes after the heat was applied. The reaction usually proceeds regularly and spreads through the whole mass which becomes more or less

liquid throughout. At the end the residue sets to a hard cake and the nitrile ceases to come off.

The lid of the iron retort was made tight by a ring of asbestos paper wet with glycerine.

The plain retort used was the ordinary plain glass retort, either 250 c.c. or 500 c.c. capacity.

The short straight tube was made of hard glass, closed at one end, about 175 mm. long and 22 mm. diameter.

The long straight tube used in the brass block method was made of soft glass, closed at one end, about 300 mm. long and 22 mm. diameter. The open end carrying the cork projected out of the block 25 mm.

The short straight tube and the brass block methods gave purer products. The iron retort gave impure products, colored more or less brown, due to dissolved iron.

The advantage of the long straight tube heated in brass block is that the whole tube is heated at the same time, not one spot at one time. The nitrile is driven over as fast as it is formed.

When the mixture is heated in the retort the nitrile remains longer in contact with the heated mass and there is more opportunity for decomposition and side reactions. The distillates from the retort are less pure and contain more free acid. The presence of water in the materials used may account for the presence of free acid in the distillate but more acid is usually found than can thus be accounted for. Some unknown side reactions must account for the most of this acid.

WORKING UP OF PRODUCTS

The methods of separating the nitriles from the crude distillates were those used in ordinary organic preparations.

The distillate containing acetonitrile or propyl cyanide was diluted with half its volume of water, treated with solid potassium carbonate or ammonia gas to saturation, the upper layer separated and fractionated. In some cases the distillate of acetonitrile was fractionated up to 85° C. and the lower fraction put through this treatment.

Propionitrile was separated by calcium chloride and then fractionated.

Isobutyl cyanide was separated by fractionation.

In the cases of stearic nitrile, cinnamic nitrile, hydrocinnamic nitrile and benzyl cyanide, the distillate was treated with a little water and a slight excess of ammonia and steam distilled. The nitrile was separated and an additional amount obtained from water layer by ether. Stearic nitrile was obtained from the crude distillate by fractionation in vacuum. It was never obtained entirely pure.

The distillate containing terephthalic nitrile was purified by sublimation. This gave beautiful short white needle shaped crystals, mpt. about 200° C.

EXPERIMENTS

The following gives the results of the experiments collected in tabular form. For the sake of simplicity and compactness the results are collected under the formula of the salt used. The numbers of the experiments give the order in which they were made. All weighings in the first few experiments were made on an ordinary laboratory balance, in the later experiments on a balance barely sensitive to 0.01 gram.

The first column gives the numbers of experiments.

The second column gives the formulae of the constituents of the mixture and the figures under each formula represent the weights used in grams.

The third column gives the actual time of the experiments, from the moment heat is applied until it is withdrawn.

The fourth column gives the weight of the crude distillate obtained.

The fifth column gives the calculated weight of nitrile and the sixth, the weight obtained on purification and the seventh, the yield in percent of calculated.

1. No.	2. Composition of Mixture		3. Time In Min.	4. Crude Prod.	5. Nitrile Calc.-Found	6	7. % Yield
	$Pb(CNS)_2$	$Zn(C_{17}H_{35}COO)_2$					
1.	51	100	90	52	84 - 16		19
2.	60	60	120	50	50 - 5.		10
48	30	50	45	40	42 - --		--
49	15	25	45	22	21 - 20		95.2
	$Pb(CNS)_2$	$Pb(C_6H_5CH_2COO)_2$					
3	35	50	120	15	24.5- 6		24.5
	$Pb(CNS)_2$	$Zn(C_6H_5CH_2COO)_2$					
11	45	40	90	21	29.7 -15		50.5
	$Pb(CNS)_2$	$Pb(C_6H_5CH:CHCOO)_2$					
4	100	75	150	10-15	38.6 - 8		20.6
	$Pb(CNS)_2$	$Zn(C_6H_5CH:CHCOO)_2$					
6	75	50	240	-----	43.8 - 14		32
7	75	25	240	-----	21.9 - 8		36.5
8	65	25	180	8	21.9 - 6		27.4
	$Pb(CNS)_2$	$Zn(C_6H_5CH_2CH_2COO)_2$					
9	35	35	90	21	25.1 - 18		71.7
10	50	25	60	19	17.9 - 12		67
	$Pb(CNS)_2$	$Zn(CH_3CH_2CH_2COO)_2$					
12	35	18	150	10	10.39 - 3		28.8
41	4.5	3	90	1.5	2.1 - 1.3		60.7
50	30	15	120	8.9	8.6 - 5.3		61.6

No.	Composition of Mixture		Time In Min.	Crude Prod.	Nitrile Calc.-Found	% Yield
	$KCNS$	$Ca(CH_3COO)_2$				
5	75	25	----	1.2*		
	$Pb(CNS)_2$	$Pb(CH_3COO)_2$				
13	120	120	240	28	30.3 - 5	16.5
15	85	83	90	22	20.9 - 6	28.6
16	95	85	150	21	21.5 - 6	27.9
	$Pb(CNS)_2$	$Zn(CH_3COO)_2$	(Calc. ratio 1:1.81)			
18	90	50	210	23	22.4 - 9	40.2
19	72	20	120	11	8.95- 4	44.7
20	115	60	195	28	26.8 - 15.5	57.3
26	4	2	30	.4	.895- .2	22.4
33	50	25	150	7.	11.2 - 1.4	12.5
35	11	5	75	1.4	2.2 - .56	25.4
36	18	10	180	3.	4.5 - 1.*	22.2
37	6	3	60	1.5	1.3 - .8	61.5
38	6	3	60	1.2	1.3 - .3	23.7
39	6	3	180	.6	1.3 - .3	23.7
43	40	20	180	7.4	8.95- 4.1	45.7
44	100	50	420	19.8	22.4 - 11.3	50.5
45	140	70	420	26.5	31.3 - 17.8	56.8
	$CuCNS$	$Zn(CH_3COO)_2$				
34	3	4	30	.8	1.8 - .4	22.2
	$Zn(CNS)_2$	$Zn(CH_3COO)_2$				
40	3	3	180	.7	1.3 - .4	30.7
	$Pb(CNS)_2$	$Cu(CH_3COO)_2$				
21	90	50	60	25	22.6 - 6	26.6

No.	Composition of Mixture		Time In Min.	Crude Prod.	Nitrile Calc.-Found	% Yield
	$Pb(CNS)_2$	$Mn(CH_3COO)_2$				
24	20	9	90	3.	4.3 - .3	70.3
31	10	4.2	45	1.1	2.0 - .5	25.0
	$Pb(CNS)_2$	$Ni(CH_3COO)_2$				
25	10	5	45	1.5	2.3 - 0.1	4.3
	$Pb(CNS)_2$	$Co(CH_3COO)_2$				
27	4	2	30	.5	.93- .2	21.6
	$Pb(CNS)_2$	$Mg(CH_3COO)_2$				
28	7	3	30	.6*		
	$Pb(CNS)_2$	$Sr(CH_3COO)_2$				
29	6	3.4	45	.3	1.4 - .3	21.4
	$Pb(CNS)_2$	$Ba(CH_3COO)_2$				
30	6.5	5	45	.8	*1.6 - .3	18.7
	$Pb(CNS)_2$	$Zn(COO)_2C_6H_4$				
22	5	3	30	1.	1.7 - 1	58.8
	$Pb(CNS)_2$	$Zn(CH_3CH_2COO)_2$				
42	5	3	120	1.5	1.56 - 1.1	70.6
	$Pb(CNS)_2$	$Zn((CH_3)_2CHCH_2COO)_2$				
46	5	3	120	1.3	1.86 - 1.	53.7
47	4	1.5	120	.9	.93 - .8	85.8

* See note

NOTES ON EXPERIMENTS

In Experiments 1, 2, 3, 4, 6 and 7 the mixture was heated in an iron retort under vacuum.

In Experiments 43, 44, 45 and 50 the mixture was heated in an iron retort without vacuum.

In Experiments 5, 8, 9, 10, 11, 12, 13, 15, 16, 18, 19, 20, 21, 33, 48, and 49 the mixture was heated in a plain glass retort without vacuum.

In Experiments 22, 24, 25, 26, 27, 28, 29, 30, 31, 34 and 35 the mixture was heated in a short straight tube with a luminous flame and finally with a non-luminous flame.

In Experiments 37, 38, 39, 40, 41, 42, 46 and 47 the mixture was heated in a long straight tube placed in a brass block, which was heated by means of two Bunsen burners .

According to Liebig and Rammelsburg[1] and also Voelckel[2] sulphocyanic acid decomposes in presence of water by heat into carbon dioxide, carbon disulphide and ammonia:

$$2HCNS + 2H_2O = CO_2 + CS_2 + 2NH_3$$

$$HCNS + 2H_2O = CO_2 + H_2S + NH_3$$

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1. Pogg. Ann. 56, 94 (1842).

2. Ibid., 58, 135 (1843).

2. Ann der Chem. u. pharm. 43, 74 (1842).

An experiment was performed to determine the effect of the decomposition products of sulphocyanic acid on the lead salt of benzoic acid. Dry ammonia was passed through carbon disulphide which was sufficiently warmed to give it the proper vapor tension. The mixture of the vapors of ammonia and carbon disulphide was passed over lead benzoate (39 grams), which was heated in an oil bath to a temperature of 220° C. Results: a mixture of benzoic acid and benzonitrile condensed on the cooler part of the lead benzoate flask and also in the condenser. A few drops of a pale yellow liquid passed through the condenser. This had an odor of carbon disulphide. All the lead benzoate was converted into a black residue of lead sulphide, with black mirror of same around the upper part of the flask. The amount of benzonitrile formed was insignificant. This shows that ready formed CS_2 and NH_3 do not account.

In Experiment 17, a mixture of ammonia and carbon dioxide was passed over a mixture of 35 grams of lead benzoate and 5 grams of sulphur, heated in an oil bath to a temperature of 240° C. Results: Solid ammonium carbonate was deposited on the walls of the lead benzoate flask and in the condenser and also in the receiver. Sulphur sublimed and deposited on the upper part of the flask. The odor of benzonitrile was apparent but the amount formed is insignificant.

In Experiment 36, to determine whether the nitrile is decomposed by side reactions, etc., into the free acid, the mixture of zinc acetate and lead sulphocyanate was heated in

an oil bath with reflux condenser. The blackening began between 150° and 170° C. and the reaction began between 250° and 255° C. At 255° C. the oil bath was removed and the heating completed with a luminous flame and the contents distilled. The yield of nitrile was not increased in this way.

In Experiments 5, 28, and 30 the crude distillate had a fearful, suffocating odor. This may be due to methyl isocyanide but its presence was not proved. Some ammonia was present.

Stannous and basic ferric acetates were tried with lead sulphocyanate but the mixtures did not fuse and gave no nitrile. In the case of basic ferric acetate a white solid was deposited in the condenser, which disappeared slowly on exposure to air and proved to be ammonium carbonate.

CONCLUSIONS

1. An excess of lead sulphocyanate does not increase the yield of the nitrile (Exps. 2, 7, 10 and 19).

2. The zinc salt of the acid gives a better yield then the lead salt. (Exps. 6, 11, 18, 19, 20, etc.)

3. The yield of nitrile is same in vacuum as at atmospheric pressure.

4. The influence of double bond is seen in the difference in yields given by cinnamic and hydrocinnamic acids, the saturated acid giving an excellent yield. (Exps. 6 and 10)

5. The method works as well for the dicarboxyl acids as for the mono-acids. (Exp. 22).

6. The results of quantitative and gas analyses show that the equation $Pb(CNS)_2 + Zn(CH_3COO)_2 = 2CH_3CN + PbS + ZnS + 2CO_2$ expresses the reaction. A little carbon monoxide was found. No free hydrogen sulphide was detected, all the sulphur being present as sulphides.

7. A satisfactory yield of acetonitrile may readily be obtained by heating a mixture of dry zinc acetate with a slight excess of lead sulphocyanate. The mixture is heated slowly in a plain glass retort till no more distillate comes over. The distillate is mixed with half its volume of water, saturated with solid potassium carbonate or ammonia gas and the nitrile separated and fractioned. Good yields of other nitriles may be obtained in a similar way.

II. CATALYTIC PREPARATION OF NITRILES

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INTRODUCTION

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Numerous experiments have recently been described, in which substances have been made to react, with elimination of water, by passing them, in vapor form, over certain metallic oxides, notably alumina and thoria. Thus Senderens[1] prepared ethers by passing vapors of the alcohols over alumina at 240-260°C. Sabatier and Mailhe[2] found that alcohols yield ethylene hydrocarbons and water with thoria and alumina at 300-350°C., and that various phenols[3] when mixed with methyl alcohol give the methyl ethers of the phenols with thoria at 390-420°C., or the diphenyl ethers[4] when the alcohol is left out. The same authors[5] found that, when a mixture of the vapors of an acid and an alcohol is passed over titania or thoria at 280°C., esterification takes place with great rapidity, the limit of esterification being reached in minutes instead of the hours required at 154° or 200° C., without catalyst.

Since the formation of a nitrile from the acid and ammonia

$$CH_3COOH + NH_3 \longrightarrow CH_3CN + 2H_2O$$

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1 - Compt. rend. 148, 227-8 (1909).

2 - Ibid., 150, 823-6 (1910).

3 - Ibid., 151, 359-62 (1910).

4 - Ibid., 151, 492-4 (1910).

5 - Ibid., 152, 494-497 and 1044-47 (1911). Chem. Zt. 35, 193 (1911).

may be regarded as a dehydration reaction, it was thought that it might take place under similar circumstances. The experiments have justified this supposition since it has been found that excellent yields of acetonitrile may be obtained directly from acetic acid and ammonia, by passing their vapors over alumina or thoria at 500°C.

The study of this reaction may throw some light on the mechanism of the other reactions since, in this case, we are well acquainted with ammonium acetate which may be formed as an intermediate product in the reaction.

Acetic acid has been the only acid studied, but it is probable that other acids will yield nitriles under similar circumstances.

As usually made, from acetamide and phosphorous pentoxide, both of which are rather expensive, acetonitrile is an expensive substance and one difficult to prepare in large quantities. By the present method in which it is made in a direct continuous process from acetic acid, and ammonia, both cheap materials, it becomes one of the most accessible compounds.

Materials

A high grade glacial acetic acid containing very near 100% acid was used. Weighed amounts of this were diluted with weighed amounts of water for the acids of 95%, 90%, etc., strength. The other chemicals used were good commercial products. The ammonia was drawn directly from a cylinder of the liquified gas.

The Catalyst

Pumice stone, broken to pieces 3 to 5 mm. in diameter, was soaked in a concentrated solution of aluminium sulphate, treated with ammonium hydroxide, and well washed. The pumice stone with the adhering aluminium hydroxide was at first dried in an air bath, but later was dried in the copper tube in a current of ammonia.

For the thoria catalyst, the pumice stone was wet with a concentrated solution of thorium nitrate and heated to about 500°C. in a current of ammonia.

Apparatus

The catalyst was placed in a very thick walled copper tube 762 mm. long and 32 mm. bore, heated by long burners. This will be more fully described elsewhere. The acid was run in through a brass tube containing a trap to prevent the exit of vapors. This ended about 80 mm. inside the copper tube so that the acid was vaporized on entering. Around this tube was a larger but shorter tube, through which the ammonia was introduced. Thus the acid vapor was introduced directly into an atmosphere of ammonia at the reaction temperature.

The exit end of the copper tube was connected through a Liebig condenser with a receiver from which a tube led to a flask of dilute sulphuric acid to absorb any excess of ammonia gas.

The temperature of the copper tube was measured by an

arrangement by which the expansion of the tube itself was made to move a hand on a dial.

Procedure

The acid or other liquid was dropped into the funnel of the trap tube from a small dropping funnel at a rate of one drop per second. The ammonia was passed in at such a rate that white vapors filled one half the condenser tube. This shows presence of sufficient excess of ammonia.

Usually the product in the receiver forms two layers, the upper one being nearly pure nitrile, and the lower containing some nitrile and much ammonium acetate. Acetonitrile is salted out of water by ammonium acetate. On completion of each experiment, the upper layer of nitrile was separated and distilled up to 85°C. The lower layer was fractionated up to 90°C., the fraction being re-distilled up to 82-84°C. The total nitrile obtained is the sum of these two portions. In cases where no layer was observed the whole product was fractionated up to 90°C., the fraction being re-distilled up to 85°C.

Results

The first experiment with alumina at above 500°C. showed the production of nitrile. Then a large number of experiments were made in order to find the best conditions as to catalyst, temperature, relative amount of ammonia, etc. The results

of these are given below in tabular form.

It was thought possible that ethylacetate might react with ammonia:

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CN + HOC_2H_5 + HOH$$

and accordingly this was tried with alumina at 510°C., but no nitrile was obtained. It is known that acetone passed over pumice at 500°C. gives ketene[1] which might possibly react with ammonia to form the nitrile.

$$CH_3COCH_3 \longrightarrow CH_2 : CO + CH_4$$
$$CH_2 : CO + NH_3 \longrightarrow CH_3CN + H_2O$$

Accordingly acetone vapor and ammonia were tried at 500°C. with alumina, but no nitrile was obtained.

It was thought that acetanhydride might give better yields with ammonia than acetic acid, since less water would have to be split off. Accordingly two experiments were tried, using the anhydride, at 500°-530° C. and at 520° — 560° C. These gave 31.3 and 24.4% of the calculated amount of nitrile. As these were lower yields than were usually obtained with the 100% acid the use of the anhydride appears to be of no advantage and no further experiments were tried with it. The anhydride would, doubtless, have given better yields with the better catalyst that was used in later work with acetic acid.

In order to ascertain whether a catalyst is required, two

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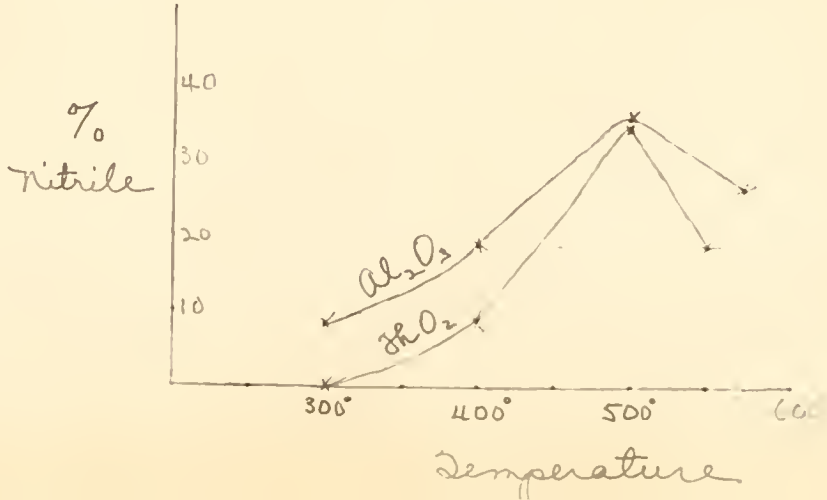
1 - Schmidlin and Bergman, Ber. d. Chem. Ges. 43, 2821 (1910).

experiments were tried in which acetic acid was passed through the hot tube filled with broken pumice stone at 400°C. and at 500°C. but no nitrile could be isolated in either case. The product seemed to be mainly acetamide.

The next experiments were to determine the activity of the two catalysts, alumina and thoria at various temperatures with 100% acetic acid. The four experiments with alumina were run with same catalyst without removing it from the copper tube and the four with thoria likewise.

TABLE I

Temp.	Acid Used	Time in minutes	With Thoria Grams	With Thoria Percent	With Alumina Grams	With Alumina Percent
305°	20 g.	----	none	----	----	----
300°	107.5	80	----	----	6.0	8.2%
405°	57.9	65	3.5	8.8	----	----
400°	118.0	65	----	----	15.0	18.6
500°	66.0	75	15.4	34.1	----	----
500°	89.0	60	----	----	21.5	35.3
550°	83.5	85	10.5	18.4	----	----
575°	120.0	55	----	----	21.8	26.6



For the lower temperatures the alumina gives decidedly better results. About 500°C. appears to be the best temperature with both catalysts. The results are plotted in curves with the percentage yield against temperature. Too much reliance must not be put in these figures, since the results given below show that there is great variation in the yields without apparent cause, and that different preparations of the same catalyst give widely different results. As the alumina appears to be slightly more effective than the expensive thoria, the alumina catalyst was used exclusively in the remainder of the work. In the experiments at 300° and 400° C. with both catalysts acetamide seemed to be present in the product, but it was not positively identified.

The remaining experiments are all given in Table II below, the two main variables being percentage of acetic acid and the preparation of the catalyst. Experiments were run with differing concentrations of the acid with one lot of catalyst, and then the copper tube would be cleaned out and another lot of catalyst put in and more experiments run. A line across the table indicates this change to a new lot of catalyst, the double line at Ex. 39 indicates change in preparation of catalyst. The temperature was near 500° in all. The experiments are numbered in the order in which they were run.

The catalyst becomes covered with a black deposit and loses its activity. The method of estimating the nitrile gives, at least, only approximate results. It represents not the amount formed, but the amount that may be isolated according to methods in use in ordinary organic preparations. The

accuracy of the work naturally increases toward the end.

TABLE II

Number of Experiments	Strength of acid	Temperature Start	Temperature End	Time in Minutes	Acetonitrile Upper Layer	Acetonitrile Lower Layer	Acetonitrile Total	Acetonitrile Calculated	Yield in percent
1	100%	500°	500°	135	----	----	14.8	41	36.1
2	"	520°	550°	99	10.7	2.2	12.9	41	31.5
3	"	510°	505°	63	16.6	4.3	20.9	41	50.2
4	"	500°	500°	42	----	----	18.4	41	43.9
5	"	510°	505°	13	----	----	10.1	41	24.7
6	90%	505°	505°	60	16.9	8.8	25.7	36.9	69.6
7	80%	500°	510°	30	11.4	3.9	15.3	32.8	46.6
8	95%	500°	505°	45	18.9	3.2	22.1	38.9	56.8
9	"	500°	500°	35	19.7	1.6	21.3	38.9	54.7
10	"	500°	500°	45	22.1	0.9	23.0	38.9	59.1
11	90%	500°	520°	35	9.6	3.4	13.0	36.9	35.2
12	"	505°	505°	60	15.6	2.5	18.1	36.9	49.0
13	"	510°	510°	55	12.2	3.1	15.3	36.9	41.4
14	"	500°	505°	35	9.8	2.9	12.7	36.9	34.4
15	"	510°	505°	45	12.0	2.7	14.7	36.9	39.8
16	85%	500°	500°	50	9.3	4.3	13.6	34.9	38.9
17	85%	525°	510°	45	11.0	4.2	15.2	34.9	43.5
18	"	505°	525°	40	12.4	3.1	15.5	34.9	44.4
19	"	505°	510°	50	15.3	2.5	17.8	34.9	51.0
20	"	510°	510°	40	12.2	3.5	15.7	34.9	44.9
21	80%	500°	510°	40	13.4	2.8	16.2	32.8	49.3
22	"	505°	510°	40	13.4	3.4	16.8	32.8	51.2
23	"	515°	510°	45	13.9	1.6	15.5	32.8	47.2

TABLE II

Number of Experiments	Strength of acid	Temperature Start	Temperature End	Time in Minutes	Acetonitrile Upper Layer	Acetonitrile Lower Layer	Acetonitrile Total	Calculated	Yield in percent
24	75%	510°	520°	45	13.2	4.1	17.3	30.8	56.2
25	"	500°	525°	55	9.1	8.2	17.3	30.8	56.2
26	"	505°	520°	65	10.5	6.6	17.1	30.8	55.5
27	70%	500°	500°	55	8.0	4.2	12.2	28.7	42.5
28	"	500°	500°	60	4.3	7.7	12.0	28.7	41.8
29	"	500°	500°	50	7.2	5.8	13.0	28.7	45.2
30	95%	500°	525°	55	13.0	3.6	16.6	38.9	42.6
31	95%	510°	520°	55	18.8	3.7	22.5	38.9	57.7
32	90%	520°	525°	65	19.9	5.3	25.2	36.9	68.3
33	"	500°	525°	65	13.8	8.5	22.3	36.9	60.4
34	85%	510°	520°	60	10.5	8.5	19.0	34.9	54.4
35	80%	500°	525°	65	----	----	16.4	32.8	50.0
36	85%	500°	525°	55	10.8	6.6	17.4	34.9	49.8
37	"	500°	520°	70	7.5	10.3	17.8	34.9	51.0
38	75%	500°	520°	50	6.6	6.6	13.2	30.8	42.8
39	"	510°	540°	60	----	----	13.8	30.8	44.8
40	"	520°	535°	50	14.9	7.0	21.9	30.8	71.1
41	"	525°	530°	55	13.6	6.9	20.5	30.8	66.5
42	95%	510°	525°	65	22.0	6.8	28.8	38.9	74.0
43	"	505°	520°	55	23.9	3.3	27.2	38.9	70.0
44	90%	500°	515°	50	16.6	5.6	22.2	36.9	60.1
45	"	500°	515°	60	18.8	4.0	22.8	36.9	61.7
46	85%	515°	525°	80	16.1	5.4	21.5	34.9	61.6
47	"	505°	520°	55	16.9	2.0	18.9	34.9	54.1
48	75%	510°	530°	60	11.1	5.6	16.7	30.8	54.2

TABLE II

Number of Experiments	Strength of acid	Temperature Start	Temperature End	Time in Minutes	Acetonitrile Upper Layer	Acetonitrile Lower Layer	Acetonitrile Total	Calculated	Yield in percent
49	100%	510°	530°	50	19.9	2.9	22.8	41.0	55.6
50	100%	505°	530°	55	25.9	8.8	34.7	41.0	84.6
51	"	505°	530°	75	31.7	3.5	35.2	41.0	85.8
52	95%	510°	520°	55	17.9	3.9	21.8	38.9	56.0
53	"	520°	520°	55	25.3	2.4	27.7	38.9	71.2
54	90%	510°	520°	60	20.5	3.7	24.2	36.9	65.5
55	"	510°	520°	50	16.3	2.0	18.3	36.9	49.5
56	85%	520°	520°	60	16.1	4.5	20.6	34.9	59.0
57	"	505°	520°	55	10.6	4.8	15.4	34.9	41.7

Discussion of Results

In Ex. 3 a small excess of ammonia was used and in Ex. 4 a much more rapid current of ammonia. The smaller amount gave 50.2% against 43.9% for the larger. This seems strange, at first sight, but the rapid current of ammonia hurries the acid vapor through the hot tube and does not give it time to react. In Ex. 5 the flow of the acid was four times as rapid as in Ex.3 and only about half as large a yield of nitrile was obtained, but twice as much nitrile per minute was formed.

A calculation as to the rapidity of the reaction is of

interest. Since 60 g. of acetic acid is 1 mole its vapor should occupy at 500°, $\frac{22.4 \times 773}{273}$ = 63 l. = 63,000 c.cm. As the bore of the tube is 32 mm., its area is 8.0 sq.cm. Dividing 63,000 by 8, we have 7,875 as length of a tube of this size required to contain the acetic acid vapor. In Ex. 50, this amount of acid vapor passed through the tube in 55 minutes, from which the linear velocity of the vapor must be 7875 ÷ 55 = 143 cm. per minute. As the length of the tube is 76.2 cm. the vapor must pass through the tube in one-half minute. This calculation has been made assuming that there is nothing in the tube but acetic acid vapor, while in the actual experiment there was more than an equal volume of ammonia. This more than doubles the linear velocity and reduces the time that any one portion of the vapor is in the tube to one-fourth of a minute or less. Hence, a mixture of acetic acid vapor and ammonia, at 500° C., in contact with alumina is 85% transformed to nitrile in less than 15 seconds. If this is the average velocity for the whole mass of vapor, the velocity of the reaction in the layers of the vapor in actual contact with the alumina must be enormous.

It appears from many experiments that the addition of moderate amounts of water to the acetic acid does not prevent the formation of the nitrile. In fact, in the earlier part of the work, it seemed that the yields were increased by the addition of water, but the later and more reliable experiments show a diminution of yield with increase of water present.. Since water has a much smaller molecular weight

than acetic acid, the molecular percentage of water in the mixture is much larger. The effect of the water is seen from Table III in which some of the experiments from Table II are presented in a different way. In the last column the yields obtained, with the diluted acids, are calculated as percents of the yield from 100% acetic acid.

TABLE III

Showing Effect of Water on Yield.

Experiment	Percent Acid	Actual Yield	Mol. % of Acid	Yield ÷ 85
50	100	84.6	100)	100%
51	100	85.8	100)	
53	95	71.2	85	83%
54	90	65.5	73	77%
56	85	59.0	63	70%

The results are as we should expect from the mass law since the rate of formation of nitrile appears to be roughly proportioned to the concentration of the acid in every case. The water found in the reaction diminishes the effect of the water initially present so that it is not surprising that the weaker acids give better yields than would be expected from the initial composition of the mixture. Good yields, 42 to 45%, were obtained with even 70% acetic acid. The

average of 8 experiments with 75% acid is 56% of nitrile which is better than any results obtained with 80% acid. It is not safe to draw too definite conclusions, as there is a large variation in the results. This variation comes partly from errors in the method of estimation of the nitrile, but mostly from slight changes of conditions in the various experiments, conditions that it is very difficult to control.

Inspection of consecutive experiments shows that the activity of the catalyst gradually diminishes with use and a jump in the yield is noticed on the introduction of a new lot of catalyst.

In one experiment, not included in the table, ammonium acetate dissolved in an equal weight of acetic acid was used instead of the acid. Only a little nitrile was obtained. In Ex. 2 the lower layer of the distillate was passed through the apparatus again, but only a small additional amount of nitrile was produced.

It appears from Table II that most of the nitrile is found in the upper layer and, when 100% acid is used, a good yield of the nitrile is obtained even when the lower layer is discarded. As we would expect, in the experiments with weaker acid, particularly the 70% acid, a larger amount, in some cases, half or more of the nitrile, is found in the lower layer.

It is intended to continue this work, particularly with the study of the formation of other nitriles.

SUMMARY

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1. It is found that acetic acid vapor, mixed with a moderate excess of ammonia and passed over alumina or thoria at 500°C., gives a large yield, up to 85%, of acetonitrile.

2. This reaction does not take place in case the catalyst is omitted.

3. The yield depends on the activity of the catalyst and may vary greatly for what appear to be trifling differences in the method of preparation of the catalyst.

4. So far as the present work goes, alumina appears to be the best catalyst and about 500°C. the best working temperature.

5. This method of preparation of acetonitrile is a continuous process requiring very little attention, and is adapted to use for the preparation of large quantities.

BIOGRAPHICAL SKETCH

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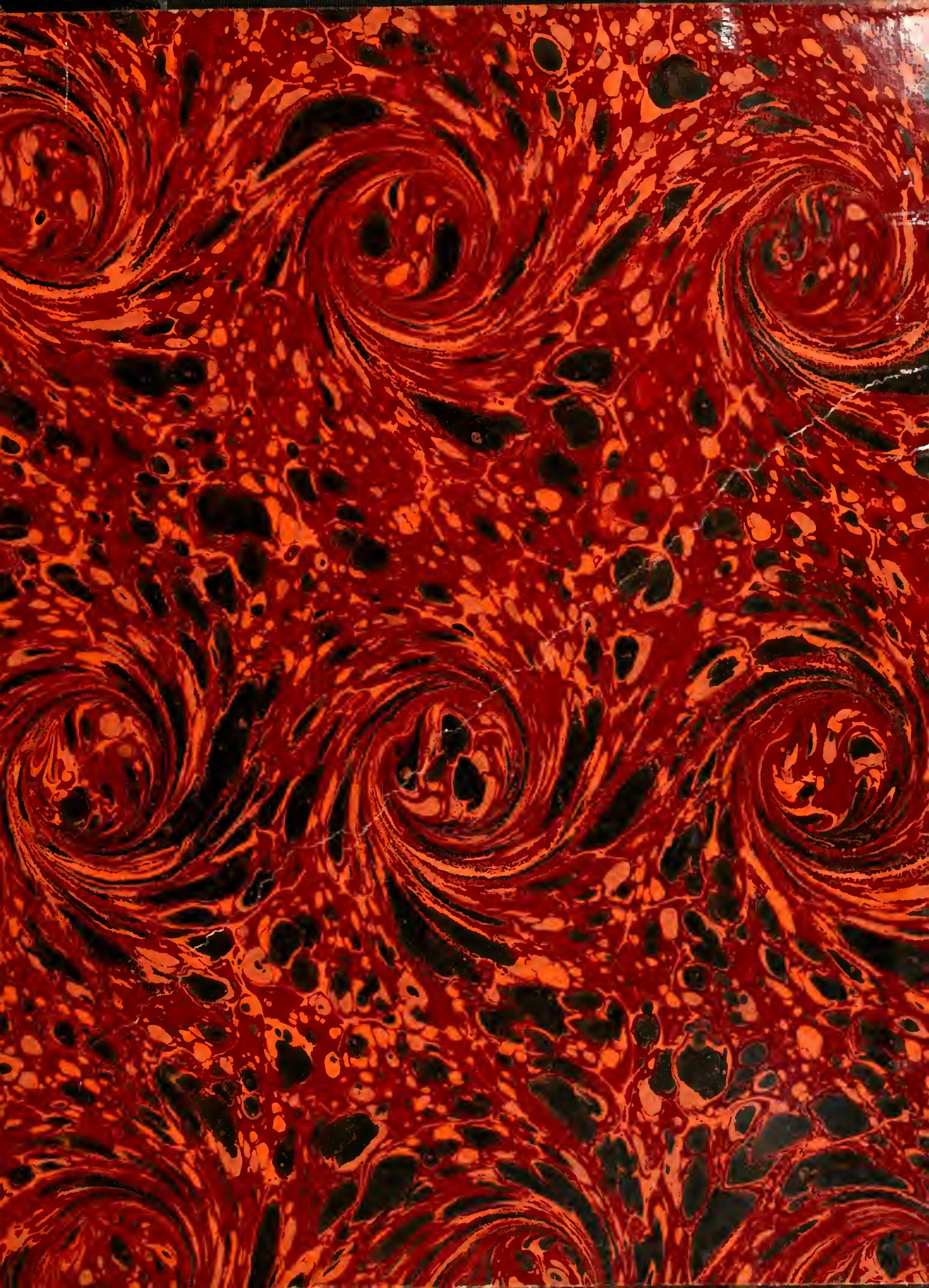
The author was born in Atlanta, Ga. in 1892. From the age of six to eleven he was taught by private tutors at home. In 1903 he entered the Marist College in Atlanta, leaving there in 1906 to enter the Wright Oral School for the Deaf in New York City. In 1909 he entered the Georgia School of Technology (a department of the University of Georgia) from which he graduated with the degree of Bachelor of Science in 1913. In the autumn of the same year he entered the Johns Hopkins University as candidate for the degree of Doctor of Philosophy. His subordinate studies were Physical Chemistry and Mineralogy. He was a Hopkins Scholar during the years, 1914-'15 and 1915-'16.